

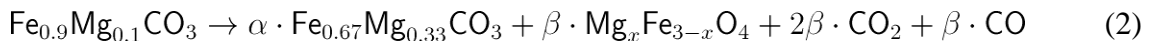
### ELECTRONIC ANNEX EA3: REASSESSMENT OF THE KOZIOL (2001) SIDERITE DECOMPOSITION STUDY

#### *Observation 1: Contraction of carbonate unit cell*

Since the unit cell volume of magnesite is slightly smaller than that of siderite, 0.279 nm<sup>3</sup> to 0.293 nm<sup>3</sup>, the contraction of the unit-cell in the residual carbonate is consistent with an enrichment of the magnesite component in the residual carbonate following partial decomposition. However, this result on its own does not provide a strong constraint on the composition of the spinel product since the fraction of reacted carbonate was not measured. Using the data of Chai and Navrotsky (1996) and references therein, the unit cell volume of siderite-magnesite solid solutions can be described as a simple linear function of the mole fraction of either end-member:

$$V_{unitcell} (nm^3) = \begin{cases} 0.279514 + 1.36044 \times 10^{-4} \cdot X_{FeCO_3} & (\text{mol. } \%) \\ 0.293118 - 1.36044 \times 10^{-4} \cdot X_{MgCO_3} & (\text{mol. } \%) \end{cases} \quad (1)$$

The most sideritic carbonate (other than pure siderite) used in these experiments was (Fe<sub>0.9</sub>Mg<sub>0.1</sub>)CO<sub>3</sub> for which the initial unit cell volume from equation (1) is 0.29176 nm<sup>3</sup>. As a consequence of partial decomposition this was reduced by 1.09% to 0.28858 nm<sup>3</sup> which corresponds to a siderite-magnesite solid solution with the composition (Fe<sub>0.67</sub>Mg<sub>0.33</sub>)CO<sub>3</sub>. Hence the decomposition reaction can be written as:



$$\text{where } 0 \leq x \leq 0.3 \begin{cases} \alpha \simeq 0.300 - 0.631 \cdot x - 1.219 \cdot x^2 \\ \beta \simeq 0.233 + 0.211 \cdot x + 0.406 \cdot x^2 \end{cases}$$

In the absence of data pertaining to the fraction of carbonate that underwent decomposition, the spinel product could have had any composition between  $\text{Fe}_3\text{O}_4$  and  $\text{Mg}_{0.3}\text{Fe}_{2.7}\text{O}_4$ .

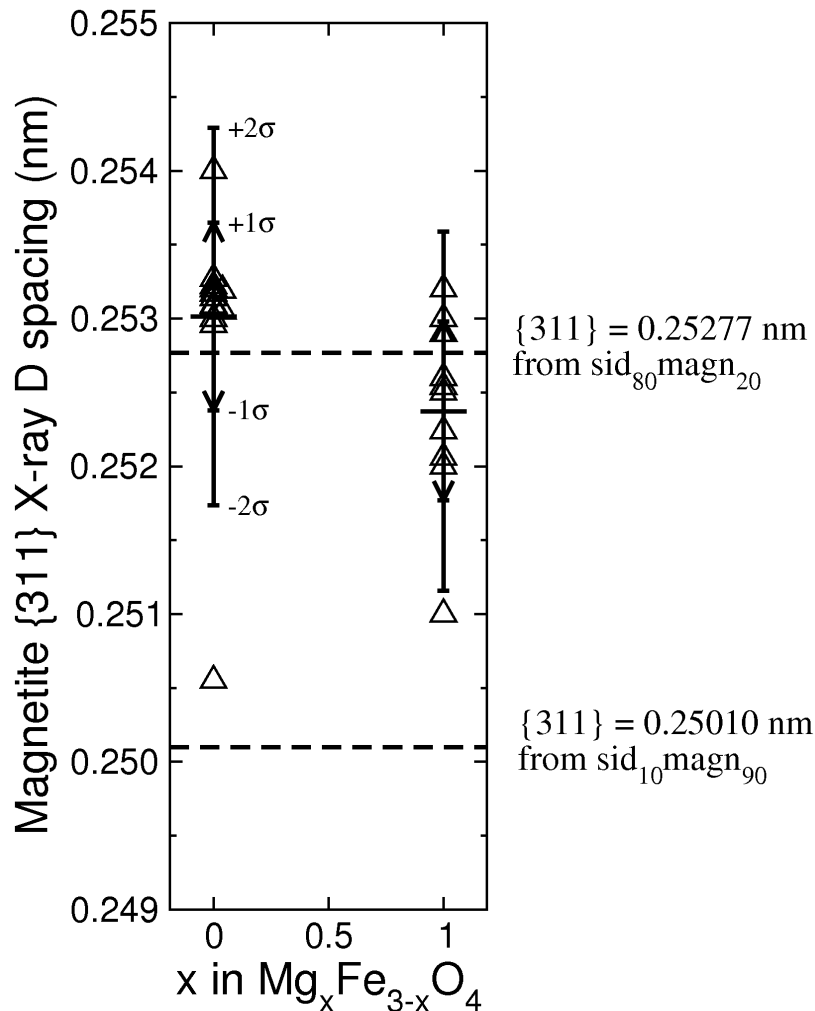
### *Observation 2: Interpretation of spinel unit cell $d$ -spacing*

Increasing the replacement of  $\text{Fe}^{2+}$  by  $\text{Mg}^{2+}$  in the spinel product (i.e.,  $\text{Mg}_x^{2+}\text{Fe}_{1-x}^{2+}\text{Fe}_2^{3+}\text{O}_4$ ;  $0 \leq x \leq 1$ ) leads to a contraction of the unit cell, and hence a reduction of  $d_{311}$  line-spacing (typically the most intense X-ray line) since for a cubic system  $d_{311} = \frac{\sqrt{3}V_{\text{unitcell}}}{\sqrt{11}}$ . For  $x = 0$  the spinel product is magnetite (i.e.,  $\text{Fe}_3\text{O}_4$ ) for which  $d_{311} \sim 0.25301 \pm 0.00064$  nm, while for  $x = 1$  the spinel product is magnesioferrite (i.e.,  $\text{MgFe}_2\text{O}_4$ ) for which  $d_{311} \sim 0.25237 \pm 0.00061$  nm. Clearly, the maximum change in the position of  $d_{311}$  line can only be on the order of  $\sim 0.25\%$ , yet the value reported by Koziol (2001) is on the order of  $\sim 0.87\%$ . This incongruity arises from the anomalously low value of the  $d_{311}$  line position reported for the partial decomposition of  $(\text{Fe}_{0.1}\text{Mg}_{0.9})\text{CO}_3$ . No Mg-spinels with  $d_{311}$  line at or near 0.25010 nm are listed in the International Centre for Diffraction Data Powder Diffraction Database (PDF-2 Release 1998)<sup>1</sup>, Fig. EA-3-1, suggesting that this line has been misidentified. In regard to this we note that the  $d$  spacing of the  $\{006\}$  line for carbonate has a value of  $d_{006} = \frac{c}{6}$ , where  $c$  is the long axis of the trigonal carbonate unit cell. Again using the data of Chai and Navrotsky (1996) and references therein, the  $c$  axis for the siderite-magnesite solid solution series varies linearly between end members and has the form:

$$c = \begin{cases} 1.50225 + 3.60013 \times 10^{-4} \cdot X_{\text{FeCO}_3} \\ 1.53825 - 3.60013 \times 10^{-4} \cdot X_{\text{MgCO}_3} \end{cases} \quad (3)$$

<sup>1</sup> <http://www.icdd.com/translation/pdf2.htm>

Hence, for a  $(\text{Fe}_{0.1}\text{Mg}_{0.9})\text{CO}_3$  carbonate  $c = 1.5059$  nm giving a  $d_{006}$  line spacing of 0.2510 nm, suggesting the 0.25010 nm line reported by Koziol (2001) for the  $d_{311}$  line of magnetite may in fact simply be the  $d_{006}$  line of the undecomposed starting carbonate.



**Fig. EA-3-1.** X-ray spacing of the  $d_{311}$  line of for magnetite ( $\text{Fe}_3\text{O}_4$ ) and the  $\text{Mg}^{2+}$  substituted isostructural homolog magnesioferrite ( $\text{MgFe}_2\text{O}_4$ ). Triangles represent all values reported for the  $d_{311}$  spacing in both magnetite (21 cards;  $0 \leq x \leq 0.04$ ) and magnesioferrite (11 cards) from the International Centre for Diffraction Data Powder Diffraction Database -- PDF-2 release 1998. The  $\pm 1\sigma$  and  $\pm 2\sigma$  deviations from the mean for values from PDF-2 release 1998 are indicated by the error bars. The dashed lines represent the values reported by Koziol (2001) for  $d_{311}$  line of magnetite produced by solid solution siderite-magnesite carbonates with siderite<sub>80</sub>magnesite<sub>20</sub> and siderite<sub>10</sub>magnesite<sub>90</sub> compositions.

## REFERENCES

- Chai, L. and Navrotsky, A. (1996) Synthesis, characterization and enthalpy of mixing of the (Fe,Mg)CO<sub>3</sub> solid solution. *Geochim. Cosmochim. Acta* **60**, 4377-4383.
- Koziol, A. M. (2001) A siderite-magnesite decarbonation study. *Geological Society of America National Meeting*, Boston, #25840 (abstr.).